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WATER SURFACANT NO. 3, STUDY NUMBER 32. REPORT OF A STUDY CONDUCTED BY ANALYTICAL REFERENCE SERVICE

Raymond J. Lishka, et al

Public Health Service
Cincinnati, Ohio

1968

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Urban and Industrial Health

WATER SURFACTANT NO. 3

STUDY NUMBER 32

ANALYTICAL REFERENCE SERVICE

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U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

Public Health Service

WATER SURFACTANT NO. 3

Study Number 32

Report of a Study Conducted by

ANALYTICAL REFERENCE SERVICE

Raymond J. Lishka and John H. Parker
TRAINING PROGRAM
National Center for Urban and Industrial Health

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Bureau of Disease Prevention and Environmental Control
Cincinnati, Ohio 45202
1968

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Public Health Service Publication No. 999-UIH-11

FOREWORD

The Analytical Reference Service (ARS) is conducted by the Training Program of the National Center for Urban and Industrial Health to evaluate laboratory methods in the environmental field. Cooperative studies by member organizations, who analyze identical samples and critically review methodology, provide the mechanism for:

> Evaluation of analytical procedures, including precision and accuracy, by comparison of the procedures and results reported by participating laboratories.
>
> Exchange of information regarding method characteristics.
>
> Improvement or replacement of existing methods by development of more accurate procedures, and development of new methodology for determination of new pollutional compounds

Samples are designed to contain measured amounts of selected constituents. Decisions as to qualitative makeup are made by the ARS staff, the membership, and consultants. Notice of each study is sent to the entire membership. To those who desire to participate, a portion of the study sample is sent, along with data forms for reporting numerical values, a critique of the procedures used, comments on modifications, sources of error, difficulties encountered, or other pertinent factors. The results and comments received are compiled, and a report of each study is prepared.

Initially directed toward examination of water, studies now include air, milk, and food. Some studies are periodically repeated for the advantage of new members, to evaluate new methods, or to reevaluate existing methods.

The selection of studies is guided by the responses to questionnaires periodically circulated among the membership, which now includes 288 Federal, state, and municipal agencies; industries; universities; consulting firms; and foreign agencies.

James P. Sheehy, Chief
Training Program

STUDIES COMPLETED AND REPORTED

Water-Minerals	Calcium, magnesium, hardness, sulfate, chloride, alkalinity, nitrite, nitrate, sodium, and potassium. Studies completed in 1956, 1958, and 1961.
Water-Metals	Lead, copper, cadmium, aluminum, chromium, iron, manganese, and zinc. Studies completed in 1957 and 1962. These same metals plus silver. Study completed in 1965. Except for the substitution of magnesium for aluminum, these same metals were analyzed by atomic absorption in 1967.
Water-Fluoride	Fluoride in the presence and absence of interferences, with and without distillation by a specified procedure. Studies completed in 1958 and 1961.
Water-Radioactivity	Gross beta activity. Studies completed in 1959 and 1961. Gross beta and strontium-90 activity. Study completed in 1963.
Water-Surfactant	Surfactant in various waters. Studies completed in 1959, 1963, and 1968.
Water-Oxygen Demand	Biochemical oxygen demand and chemical oxygen demand. Study completed in 1960. Chemical oxygen demand. Study completed in 1965.
Water-Trace Elements	Arsenic, boron, selenium, and beryllium. Study completed in 1962. These same metals plus vanadium. Study completed in 1966.
Freshwater Plankton	Evaluation of the precision and accuracy obtainable by the use of various methods of plankton counting and identification. Study completed in 1964.
Water-Nutrients	Silicate, phosphate, ammonia nitrogen, organic nitrogen, and nitrate nitrogen. Study completed in 1966.

Water-Phenols	Phenol and 2,4-dichlorophenol in water by two specified methods. Study completed in 1966.
Water-Cyanides	Potassium cyanide and potassium ferricyanide in water by two specified methods. Study completed in 1967.
Air-Inorganics	Chloride, sulfate, fluoride, and nitrate in aqueous solution and on glass-fiber, high-volume filter mats. Study completed in 1958.
Air-Lead	Filter paper tape impregnated with lead. Study completed in 1960.
Air-Particulates	Microscopic identification of some common atmospheric particulates. Study completed in 1964.
Air-Sulfur Dioxide	Sulfur dioxide in air by a specified method. Study completed in 1963.
Water-Pesticides	Lindane, heptachlor epoxide, DDE, and dieldrin in water. Study completed in 1965. Lindane, heptachlor, aldrin, heptachlor epoxide, p,p'-DDE, dieldrin, endrin, o,p'-DDT, p,p'-DDT and methoxychlor in water. Study completed in 1968.
Food-Pesticides	DDT in milk. Study completed in 1962. Lindane, heptachlor epoxide, DDE, and dieldrin in milk. Study completed in 1965.

PREFACE

Replacement by the soap and detergent industries of the branched chain alkyl benzene sulfonate (ABS) during the middle of 1965 with the more biodegradable linear alkylate sulfonate (LAS) necessitated the development by The Soap and Detergent Association of a new reference material. As developed, this reference material is typical of LAS surfactants in commercial use. For reasons of greater stability, the reference material has been prepared as the free acid rather than the sodium salt as was formerly the case when ABS was used as the reference material. In this report, however, the term LAS refers to the sodium salt (linear alkylate sulfonate) since in order to obtain consistency in reporting all values (except the raw data in Appendix A) have been multiplied by the factor 1.069; the ratio of the molecular weight of the sodium salt (338) to the molecular weight of the free acid (316). Thus, the 2.75 mg/liter of LAS acid in sample 1 has become 2.94 mg/liter of LAS sodium salt, 0.45 mg/liter of LAS acid in sample 2 has become 0.48 mg/liter of sodium salt, and 0.25 mg/liter of LAS acid in sample 3 has become 0.27 mg/liter of LAS sodium salt. Since this new LAS reference material, like ABS, is methylene blue reactive, it has been assumed that the methylene blue method in the 12th edition of Standard Methods for the Examination of Water and Wastewater was applicable. Since the two substances, however, are not identical, it became obvious that, if LAS was to be measured, a new calibration curve would have to be constructed, with the use of the new LAS reference surfactant, and it would be necessary to reevaluate the precision and accuracy of the procedure. This study has been conducted for that purpose.

Earl F. McFarren, Chief
Analytical Reference Service

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ACKNOWLEDGMENTS

This study was undertaken at the suggestion of Michael Taras, Chairman of the Joint Editorial Board of Standard Methods, in order to determine whether the old methylene blue procedure for ABS was equally applicable to the determination of the new biodegradable LAS surfactants.

Mr. T. E. Brenner, Research Director, Technical and Materials Division, The Soap and Detergent Association, supplied each participant with the LAS reference samples necessary for this study.

Dr. Robert L. Bunch, Biological Treatment Research, Cincinnati Water Laboratory, Federal Water Pollution Control Administration, reviewed the report and suggested some technical changes which were adopted.

With permission of the American Public Health Association, the methylene blue procedure for surfactants was copied from Standard Methods for the Examination of Water and Wastewater and copies were sent to each participant for use in analysis of the samples.

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PARTICIPANTS IN THIS STUDY

Alabama State Department of Public Health, Montgomery
Alabama Water Improvement Commission, Montgomery
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Arizona State Department of Health, Phoenix
Armco Steel Corporation, Middletown, Ohio
Beaumont Health Department, Texas
Calgon Corporation, Pittsburgh, Pennsylvania
California State Department of Public Health, Berkeley
California State Department of Public Health, Los Angeles
California Water Service Company, San Jose
Charlotte Water Department, North Carolina
City of Amarillo, Water Reclamation Department, Texas
City of Erie, Bureau of Water, Pennsylvania
City of Flint, Water Plant, Michigan
City of Philadelphia, Water Department, Pennsylvania
City of Seattle, Water Department, Washington
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Massachusetts Department of Public Health, Amherst
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Metropolitan Sanitary District of Chicago, Cicero, Illinois
Metropolitan Utilities District, Omaha, Nebraska
Metropolitan Water District of Southern California, La Verne
Metropolitan Water, Sewerage, and Drainage Board, Sydney, Australia
Ministere de la Sante, Montreal, Ontario, Canada
Minneapolis Water Department, Minnesota
Minnesota Department of Health, Minneapolis
Missouri Division of Health, Jefferson City
Missouri Division of Health, St. Louis
Nassau County Department of Health, Hempstead
New Hampshire Water Supply and Pollution Control Commission, Concord
New Jersey State Department of Health, Trenton
New Mexico State Bureau of Mines, Socorro
New York City Department of Health, New York
New York State Conservation Department, Scottsville
New York State Department of Health, Albany
North Carolina Department of Water and Air Resources, Raleigh
North Dakota State Department of Health, Bismarck
North Jersey District Water Supply Commission, Wanaque, New Jersey
Ohio Department of Health, Columbus
Ontario Water Resources Commission, Rexdale, Ontario, Canada
Orange County Department of Agriculture, Anaheim, California
Oregon State Sanitary Authority, Portland
Osaka City Institute of Hygiene, Japan
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Philadelphia Suburban Water Company, Bryn Mawr
Procter and Gamble Company, Cincinnati, Ohio
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Regional Environmental Health Laboratory, McClellan AFB, California
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South Carolina Pollution Control Authority, Columbia
Springwells Filtration Plant, Dearborn, Michigan
Tennessee Stream Pollution Control Board, Nashville

Tennessee Valley Authority, Chattanooga
Texas State Department of Health, Austin
United Kingdom Atomic Energy Authority, Didcot, Berks, England
USDI, FWPCA, AWTR Research Activities, Pomona, California
USDI, FWPCA, Alaska Water Laboratory, College
USDI, FWPCA, Analytical Quality Control, Cincinnati, Ohio
USDI, FWPCA, Hudson-Champlain Project, Metuchen, New Jersey
USDI, FWPCA, Kerr Research Center, Ada, Oklahoma
USDI, FWPCA, Physical Sciences, Cincinnati, Ohio
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USDI, Geological Survey, Columbus, Ohio
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University of Arizona, Tucson
University of Beograd, Yugoslavia
Utah State Division of Health, Salt Lake City
Virginia State Water Control Board, Richmond
Washington State Department of Health, Seattle
Wastewater Analysis Corporation, Trenton, Michigan
West Virginia Department of Natural Resources, Charleston
Wisconsin State Laboratory of Hygiene, Madison

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ABSTRACT

In this study each participant was shipped three sterilized water samples in disposable 1-quart polyethylene containers. Sample 1 was composed of filtered river water containing 2.94 mg/liter LAS. Sample 2 was tap water containing 0.48 mg/liter LAS. Sample 3 was distilled water containing 0.27 mg/liter LAS. A small amount of methylene blue and a copy of the procedure were sent with the samples. The data indicate no difference in methylene blue obtained from many different suppliers. Results from 111 analysts show good accuracy and precision for all samples. The standard deviations agree closely with those quoted in the 12th edition of Standard Methods for the Examination of Water and Wastewater, for the measurement of ABS by the same procedure.

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WATER SURFACTANT NO. 3

DESIGN OF THE STUDY

To prepare Sample 1, water was obtained from the Little Miami River at Cincinnati, Ohio, and allowed to age for 2 days to permit biodegradation of any residual LAS. When analysis failed to show any surfactant, the sample was chemically sterilized by adding mercuric chloride to provide a concentration of 20 mg/liter mercury. The following day the sample was filtered to remove algae and sediment. The sample was then dosed to contain 2.94 mg/liter LAS, with the same standard LAS solution that was supplied to the participants by The Soap and Detergent Association for use as a standard reference material.

Sample 2 was composed of Cincinnati tap water, sterilized with mercuric chloride in the same manner and dosed to contain 0.48 mg/liter LAS.

Sample 3 was merely distilled water, sterilized, and dosed to contain 0.27 mg/liter LAS to provide a sample with no interference.

After the samples were analyzed by different analysts and the concentrations of LAS confirmed, the samples were packaged in 1-quart disposable polyethylene containers and shipped to the participants, together with a copy of the procedure to be evaluated (methylene blue method, page 297, Standard Methods for the Examination of Water and Wastewater, 12th edition, 1965), a small vial of methylene blue, an instruction sheet, duplicate report forms, and a return envelope.

TREATMENT OF THE DATA

On receipt of the results of analysis from each participant, the data were reviewed and coded for transfer to punch cards. The data were then key-punched and analyzed by electronic computer for normality of distribution and rejection of outliers. Data received after computer analysis had begun do not appear in this report.

The data present in Appendix A are the raw data as received from the participants. However, in the summary tables and bar graphs in the main body of this report all values have been multiplied by a factor of 1.069 to convert the results from the free acid to the sodium salt, in order to obtain consistency with results previously reported when ABS was the reference material.

The data were statistically analyzed by computer for precision and accuracy. The results obtained by using the methylene blue (Eastman No. P573) provided with the sample were considered method 1, and results

obtained with the participant's methylene blue were considered method 2. The two methods were compared by computer by applying the "Student's" t-test and the F-test to the data to test for a statistically significant difference in the means and the standard deviations obtained by the two methods.

Bar graphs (Figures 1 through 6) provide a pictorial display of the data; rejected values are indicated by broken bars.

One hundred and eleven laboratories participated in this study, but one analyst commented that both sets of his results were obtained by using a standard curve developed from his own methylene blue. Therefore, his method 1 results were invalid and were not used. Four participants did not submit method 2 results.

DISCUSSION OF RESULTS

Sample 1, 2.94 mg/liter LAS in river water (Table 1, Figures 1 and 2)

One hundred and ten laboratories analyzed this sample by method 1, and 107, by method 2. The accuracy of both methods was excellent, as shown by the relative errors of 1.52 percent and 1.95 percent. The precision, as indicated by the relative standard deviations of 9.51 percent and 9.64 percent, was likewise excellent. This sample, being river water,

Table 1. Summary of Results

Sample 1, 2.94 mg LAS/liter

	Methylene blue provided	Participant's methylene blue	Overall
Number of results	110	107	217
Number of outliers	6	4	12
Mean	2.99	3.00	2.98
95% Confidence limits	±0.06	±0.06	±0.04
Mean error	+0.045	+0.057	+0.042
Standard deviation	0.284	0.289	0.272
Relative error	1.52	1.95	1.43
Relative standard deviation	9.51	9.64	9.12
95% Tolerance limits	0.63	0.64	0.58

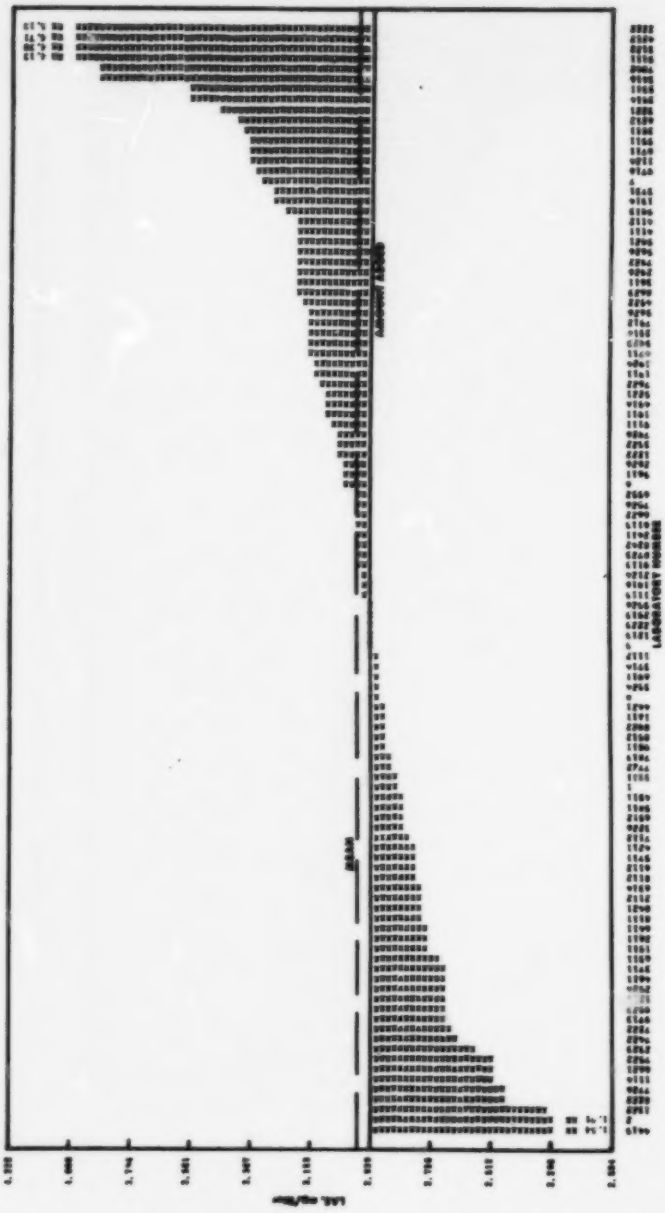

Figure 1. Bar graph for sample 1 in which the methylene blue provided was used.

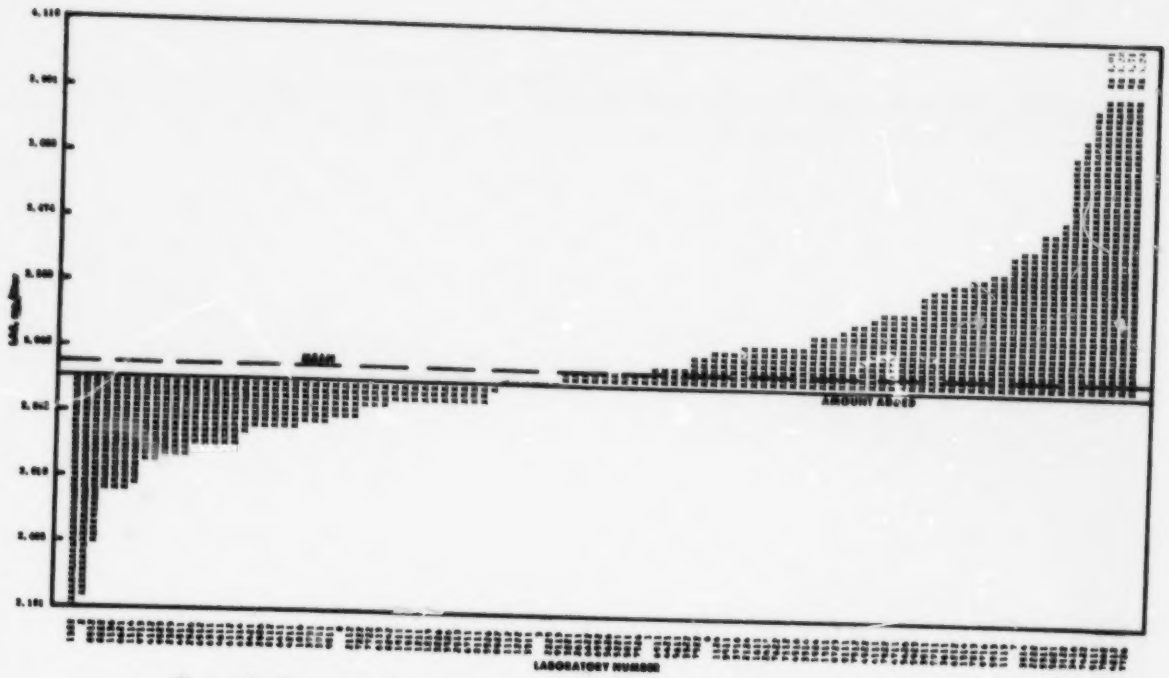

Figure 2. Bar graph for sample 1 in which participant's methylene blue was used.

would be likely to contain interfering materials, but it is evident that no difficulty was encountered in the analysis. There was no significant difference between the methylene blue furnished with the sample and the participant's own methylene blue.

Sample 2, 0.48 mg/liter LAS in tap water (Table 2, Figures 3 and 4)

One hundred and ten laboratories analyzed this sample by method 1, and 107, by method 2. The accuracy and precision were essentially the same as for sample 1, as shown by the relative errors of 1.52 percent and 0.64 percent and the relative standard deviations of 9.90 percent and 11.63 percent. Very little interference would be expected in this type of sample, and it is evident that none was encountered. No significant difference was found between the provided methylene blue and the participant's own dye.

Table 2. Summary of Results

Sample 2, 0.48 mg LAS/liter

	Methylene blue provided	Participant's methylene blue	Overall
Number of results	110	107	217
Number of outliers	7	7	17
Mean	0.49	0.48	0.49
95% Confidence limits	±0.01	±0.01	±0.01
Mean error	+0.007	+0.003	+0.006
Standard deviation	0.048	0.056	0.048
Relative error	1.52	0.64	1.27
Relative standard deviation	9.90	11.63	9.94
95% Tolerance limits	0.11	0.13	0.10

Sample 3, 0.27 mg/liter LAS in distilled water (Table 3, Figures 5 and 6)

One hundred and ten laboratories analyzed this sample by method 1, and 107, by method 2. The analyses appear less accurate for this sample since the relative errors are 10.84 percent and 10.36 percent. The precision also appears to be less since the relative standard deviations are 15.39 percent and 14.22 percent. When the magnitude of the actual amount present is considered, however, the analyses appear satisfactory.

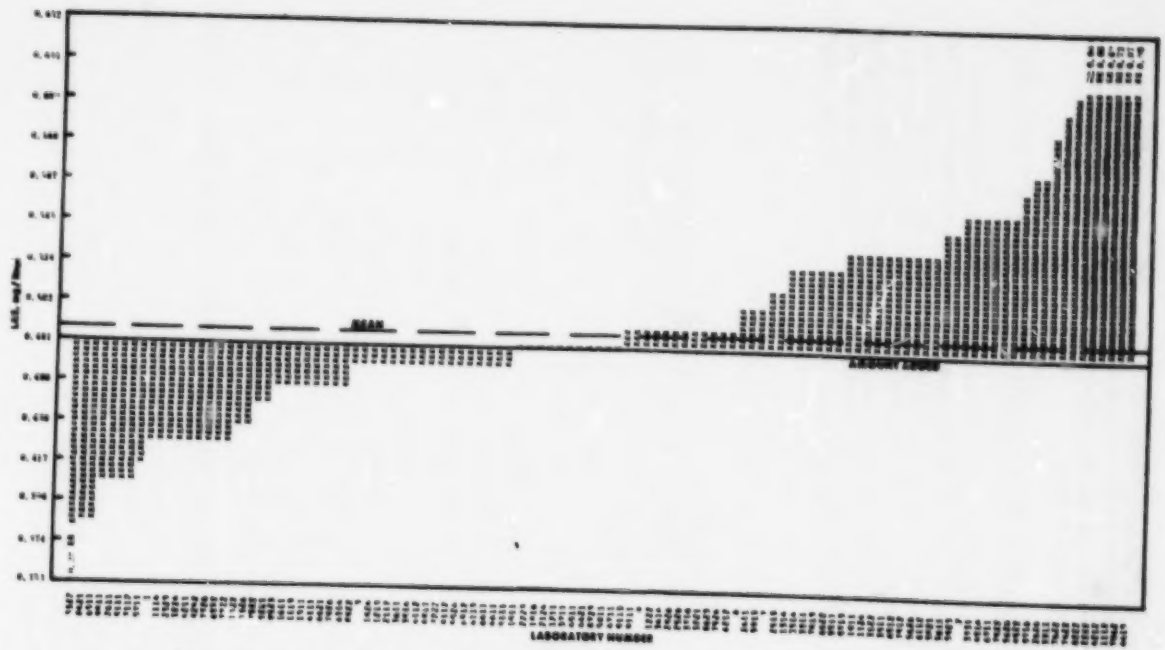

Figure 3. Bar graph for sample 2 in which the methylene blue provided was used.

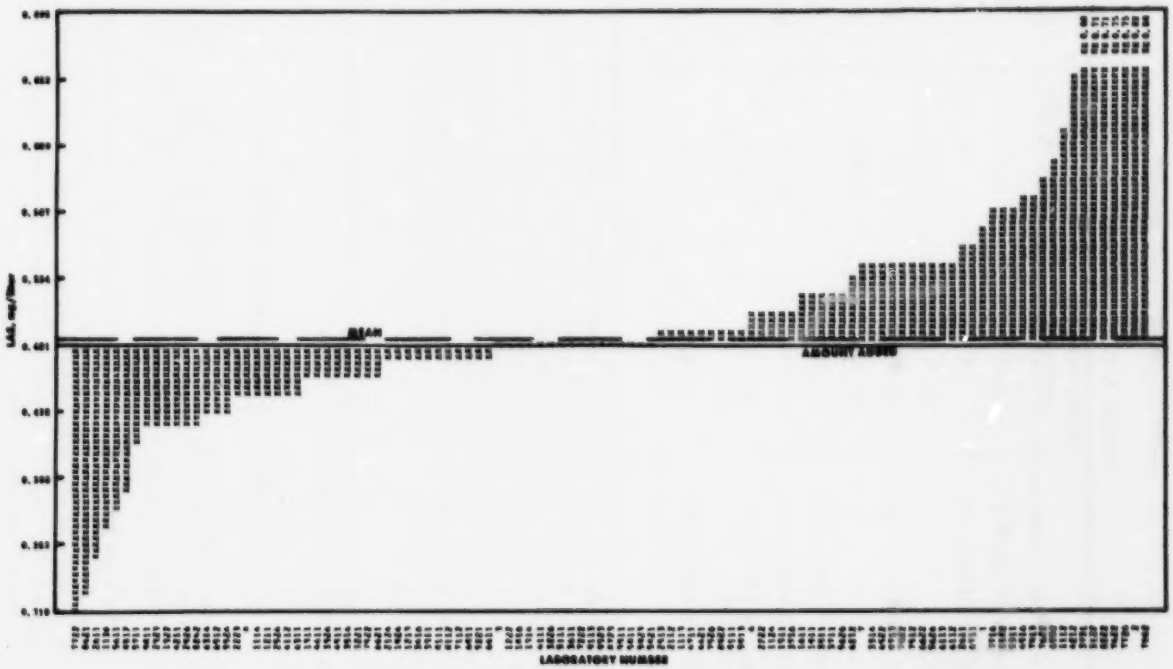

Figure 4. Bar graph for sample 2 in which participant's methylene blue was used.

Table 3. Summary of Results

Sample 3, 0.27 mg LAS/liter

	Methylene blue provided	Participant's methylene blue	Overall
Number of results	110	107	217
Number of outliers	3	2	5
Mean	0.24	0.24	0.24
95% Confidence limits	±0.01	±0.01	±0.01
Mean error	-0.029	-0.028	-0.028
Standard deviation	0.037	0.034	0.036
Relative error	10.84	10.36	10.58
Relative standard deviation	15.39	14.22	14.77
95% Tolerance limits	0.08	0.08	0.08

The apparent tendency toward slightly low results suggested instability of the sample. The ARS staff, however, analyzed all three samples 3 months after preparation and obtained values of 2.92 mg/liter for sample 1, 0.48 mg/liter for sample 2, and 0.26 mg/liter for sample 3, which indicates good stability for all three samples. A possible reason for low results for sample 3 may be the insufficient rinsing of the glass wool after filtering the chloroform extract. Another possibility may be the insufficient shaking of the sample container before removing the aliquot for analysis, as some adsorption of LAS on the container walls may occur.

No significant difference was found between the provided methylene blue and the participant's own dye.

COMMENTS OF THE PARTICIPANTS

1. "Our Methylene Blue was the general purpose reagent provided by Messrs. Hopkin and Williams, Ltd. It gave a calibration curve virtually identical to that obtained using the ARS Methylene Blue."

2. "The ARS Methylene Blue produced optical density readings 4% lower than ours which is some years old. Using our methylene blue, unreported subsequent repeat tests gave good agreement on sample #3, poorer on sample #2, and a range between 2.45 and 3.15 mg/l on sample #1."

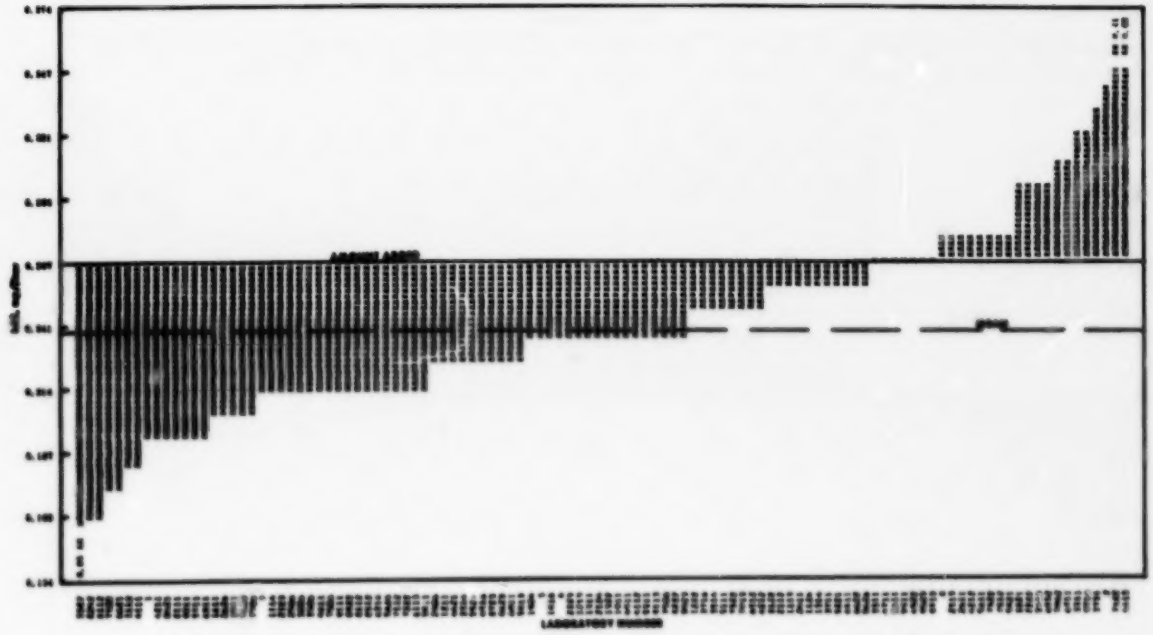

Figure 5. Bar graph for sample 3 in which the methylene blue provided was used.

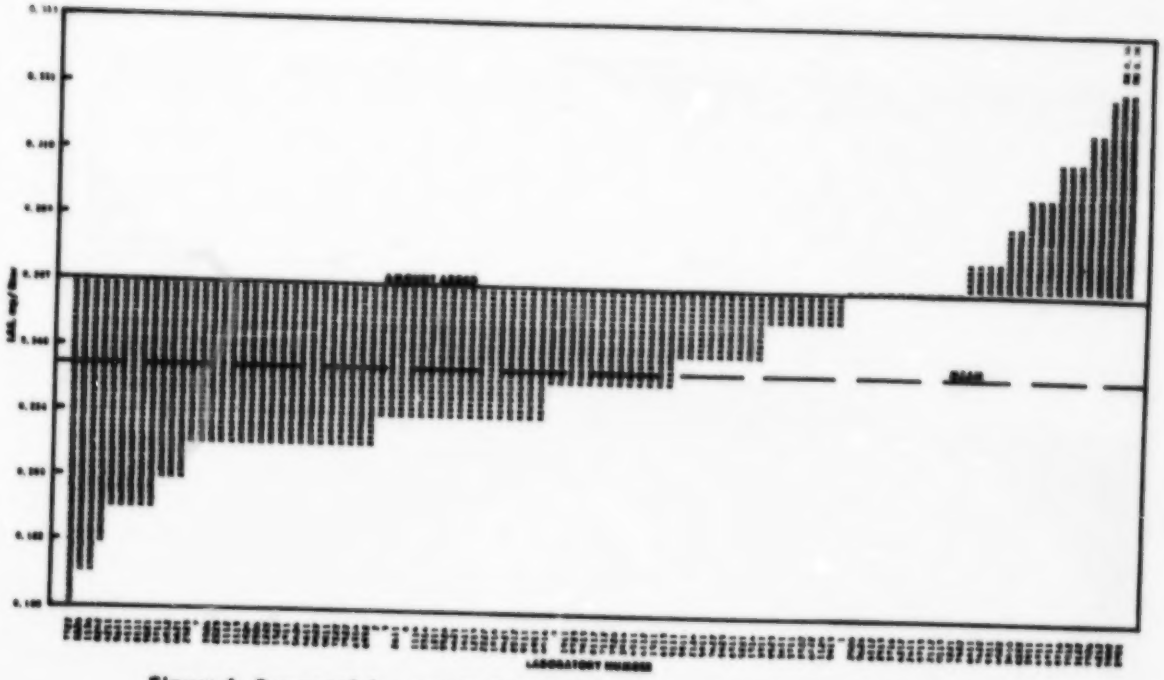

Figure 6. Bar graph for sample 3 in which participant's methylene blue was used.

3. "In the provided method I suggest that a change be made to specify that a blank, using 100 ml of distilled water be run with each batch of samples. In the preparation of the calibration graph, the 0.0 ml of standard LAS solution is in fact a blank and if the absorbance of this is subtracted from the other standards, the calibration curve can be drawn through the origin. The use of a blank will compensate for any apparent LAS present in the reagents used for subsequent analysis, which might be different from those used for the preparation of the calibration graph."

4. "Own Methylene Blue was purchased from the British Drug Houses, Ltd., approximately 10 years ago. No problems. Color was determined on Spectronic 20, at 625 mμ."

5. "Our Methylene Blue was Merck 4815 U.S.P."

6. "We had not previously used this determination. In the calibration it was a little difficult to decide on the position of the line for the Beer's Law curve, as there was some scatter of the points. No differences were apparent in the calibrations with the two samples of methylene blue. In addition to using a DK-2 spectrophotometer at 625 mμ, a filter photometer (red filter) was also employed for comparison. The two appeared to yield similar accuracies and results. We were not entirely clear as to the meaning of the concentration in the LAS solution supplied, which was quoted to contain 4.045% of LAS acids. As suggested, in diluting the solution, a proportion of the material supplied was weighed out and made up to volume. For the subsequent calculations, it has been assumed that 100 g of the LAS solution contained 4.045 g of LAS acids. In this country, sodium dihydrogen phosphate seems only to be supplied as the dihydrate. Hence, where 50 g of the monohydrate was specified, 56.5 g of the dihydrate was used."

7. "No difficulty encountered. A good standard curve was achieved."

8. "The Methylene Blue supplied with the samples had more of a purple tinge to it than our Methylene Blue. Our sample had much more blue color to it than the one furnished us."

9. "Color developed by suggested standards was too high to read. The standard range we used was from 0.03 mg/l up to 0.13 mg/l."

10. Hilger Absorptiometer used instead of Spectrophotometer, light path of 4.0 cm. Methylene Blue, Carlo Erba, Italy, Used."

11. "No systematic differences were noted between dye supplied and that on hand. Reproducibility of values is difficult."

12. "Standard curve was not a straight line around 15 ml."

13. "After the second extraction of the wash solution a distinct blue ring formed between the aqua phase and chloroform. The blue color slowly dispersed back into the aqua phase."

14. "Our dye was Methylene Blue Chloride, National Aniline Division, CI No. 922."

15. "We used Matheson, Coleman & Bell 'New Methylene Blue' (Basic Blue 24). Although some of the solutions were an intense blue color, our spectrophotometers indicated no absorbance at 652 mμ." (Ed. note: methylene blue chloride = basic blue 9.)

16. "The Methylene Blue used was National Aniline & Chemical Co. Methylene Blue Chloride (Certified; 87% total dye content), and was at least 10 years old. The calibration curve was identical with the curve for the ARS Methylene Blue."

17. "Methylene Blue dries out on the walls of the 1 cm cells and cannot be rinsed off with chloroform. After each use soak the cells in 25% nitric acid to remove the methylene blue, rinse in deionized water, then with acetone to remove the water."

18. "Methylene Blue used, Merck #4815."

19. "Methylene Blue supplied by ARS apparently same as or equal to participant's Methylene Blue prepared by standard methods."

20. "The rocking technic is difficult to standardize. Therefore, the reproducibility of the calibration curve is low."

21. "The blank reading was lower with the ARS Methylene Blue."

22. "Calculated as Na LAS, rather than as the free acid. Directions for preparing the new standard for calibration are not too clear. Our Methylene Blue was Eastman Certified Stain - CI No. 922. It gave exactly the same calibration curve as the ARS Methylene Blue."

23. "20 ml of sample 1 and 100 ml each of Samples 2 and 3 taken for analysis, based on visual observation after shaking."

24. "Analysis repeated 1 week later showed lower values for 2 and 3. Did they decompose?" (Ed. note: No.)

25. "There was a great deal of variation in the results obtained for Sample 1 (20 ml used); the results for Samples 2 and 3 were fairly consistent. (250 ml used)."

26. "Methylene Blue used was obtained from George T. Gurr (London, England)."

27. "Method simple and straightforward but cumbersome preparation of standard solution (LAS)ambiguous. Best run along with standards."

28. "Good checks were obtained at low concentrations but not at high concentrations. Cotton Pluggets were used instead of glass wool because size and thickness were more readily standardized. No singificant difference was noted between the curves using different methylene blue."

29. "Reproducible results obtained when duplicate samples are run but difficult to reproduce curve on successive days – streaks of concentrated dye appeared in $CHCl_3$ layer after 1st extraction with phosphate wash solution."

30. "In procedure (4. 3), addition of NaOH followed by H_2SO_4 is vague. A pH value or range might be more useful. Use of two separatory funnels per sample apparently does not improve results."

31. "Used 20 ml No. 1, 100 ml of No. 2, 200 ml of No. 3."

32. "The zero point on the curve gave a pink color using ARS Methylene Blue – ours did not. However, the curves were about identical."

33. "The graphs obtained were not satisfactory to all concerned. One analyst thought that 'our' methylene blue gave a much better graph. With the ARS methylene blue, the blank, through the extracted procedure, was free of any residual color. A visible transfer of blue color to the wash solution was evidenced, but upon final extraction of wash solution, the color was thought to be regained with the chloroform. It is during this step that one analyst thought a variable could be introduced. It was suggested that if possible a volume of less than 100 ml be used for final dilution of extracts for greater absorbance accuracy, since many laboratories (as ours) have only a 1 cm light path in the photometer."

34. "Sample 1 - 25 ml aliquot taken. Also development of insoluble matter after first extraction; Sample 2 - 100 ml aliquot used; Sample 3 - 250 ml aliquot used."

SUMMARY AND CONCLUSIONS

One hundred and eleven laboratories analyzed three samples for surfactant, using the methylene blue procedure from the 12th edition of Standard Methods for the Examination of Water and Wastewater. A copy

of the procedure and a small supply of methylene blue (Eastman No. P573) were included with the samples. Participants were requested to analyze the samples in which the supplied methylene blue was and to perform a second analysis of the samples in which their own methylene blue was used. No difference was found between the results obtained with the methylene blue provided and the results obtained with methylene blue from a variety of suppliers.

Analysis of filtered river water containing 2.94 mg/liter LAS and tap water containing 0.48 mg/liter LAS showed excellent accuracy and precision. Analysis of the distilled water sample containing 0.27 mg/liter LAS seemed a little less accurate and precise when relative errors and relative standard deviations were compared. The mean error, however, was nearly half of the mean error for the river water sample, and the standard deviation was one-eighth. The standard deviations agree very closely with those quoted in Standard Methods, which were from a study conducted by the Analytical Reference Service in 1963 for the measurement of ABS surfactant by the same methylene blue procedure.

The procedure might be improved by specifying glass wool plugs in the stem of the funnel rather than the vague "... draw off the chloroform layer through glass wool ...". Also, the instructions for "Measurement" should include the statement, "Subtract the absorbance of the 0.00 mg/liter standard from the readings for the remaining standards and samples to place the origin of the calibration curve at zero." Alternatively, the 0.00 mg/liter standard could be used as the reference, rather than chloroform, which would accomplish the same result.

APPENDICES

APPENDIX A.

TABULATION OF RESULTS

Table A-1. Sample 1, LAS Acid (2.75 mg/liter)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
1	2.66	1	1213	2.75	1
1	2.82	2	1222	2.85	1
2	2.08	2	1222	2.75	2
2	1.79	1	1311	2.94	1
3	2.77	2	1311	2.94	2
3	2.74	1	1314	3.08	1
6	2.83	1	1314	3.11	2
6	2.88	2	1322	2.17	1
7	3.12	1	1322	2.05	2
7	3.20	2	1511	2.56	1
8	2.72	1	1511	2.70	2
8	2.64	2	1611	2.70	1
1112	2.73	1	1611	2.90	2
1112	2.75	2	1816	2.62	2
1113	3.18	2	1816	2.78	1
1113	2.78	1	1911	2.90	1
1114	2.43	2	1911	2.70	2
1114	2.35	1	1924	2.94	1
1124	3.15	1	1924	2.94	2
1124	2.88	2	2112	2.58	1
1136	2.40	2	2112	2.64	2
1211	2.70	2	2124	2.78	1
1211	2.50	1	2124	2.89	2
1213	2.70	2	2222	4.80	1

(Table A-1 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
2222	3.25	2	3314	2.93	2
2223	2.77	2	3314	2.96	1
2223	2.75	1	3322	2.85	2
2323	2.41	1	3322	2.85	1
2323	2.51	2	3326	2.70	2
2411	2.80	1	3326	2.72	1
2411	2.90	2	3416	3.65	1
2513	2.75	1	3416	3.55	2
2513	2.70	2	3511	3.18	1
2526	2.50	1	3511	3.08	2
2526	2.55	2	3514	3.20	2
2611	2.56	1	3514	3.35	1
2611	2.80	2	3611	3.09	2
2626	2.84	1	3611	3.00	1
2926	2.60	2	3711	2.62	2
2926	3.00	1	3711	2.50	1
3122	4.10	1	3716	2.89	2
3122	3.50	2	3716	2.72	1
3221	3.25	1	3731	2.62	2
3221	2.80	2	3731	3.08	1
3226	2.65	1	4111	3.00	2
3226	2.70	2	4111	3.00	1
3311	2.75	2	4112	2.50	2
3311	2.67	1	4112	3.00	1

(Table A-1 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
4211	2.60	1	5511	3.15	1
4211	2.60	2	5526	2.74	2
4212	4.41	1	5526	2.76	1
4212	4.41	2	5611	2.83	2
4415	1.44	1	5611	2.83	1
4421	2.82	2	5626	2.96	1
4421	2.71	1	5626	2.80	2
4511	2.52	2	5626	3.00	1
4511	2.65	1	5626	3.01	2
4516	2.90	1	5711	3.08	2
4516	2.90	2	5711	2.60	1
4522	2.98	2	5811	2.65	1
4522	2.98	1	5811	2.80	2
4611	2.50	1	5821	3.00	1
4611	2.55	2	5821	3.30	2
4711	2.95	1	5913	3.03	1
4711	3.00	2	5913	3.14	2
5111	3.75	2	5923	3.05	2
5111	3.87	1	5923	2.95	1
5221	2.80	2	6112	2.60	1
5221	2.90	1	6112	2.55	2
5311	3.36	1	6113	2.68	2
5311	3.26	2	6113	2.80	1
5511	2.88	2	6212	3.20	1

(Table A-1 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
6212	3.10	2	7422	3.64	2
6311	2.52	1	7512	2.96	1
6311	2.55	2	7512	2.97	2
6314	2.59	1	7522	2.85	2
6314	2.58	2	7522	2.35	1
6411	2.60	2	7526	2.81	2
6411	2.56	1	7526	2.80	1
6512	2.55	2	7622	2.91	1
6512	2.65	1	7622	2.90	2
6552	2.80	2	7722	2.68	2
6552	2.80	1	7722	2.68	1
6621	2.35	1	7726	2.30	1
6621	2.40	2	7726	4.90	2
6622	2.80	1	7813	3.12	2
6622	2.80	2	7813	2.68	1
6711	2.70	2	7862	3.66	1
6711	3.15	1	7862	4.00	2
6911	2.82	2	7922	3.00	2
6911	2.72	1	7922	3.00	1
7112	2.90	2	7926	2.85	1
7112	2.63	1	8111	2.58	1
7222	2.48	1	8111	2.70	2
7222	2.68	2	8112	2.60	2
7422	2.46	1	8112	2.60	1

(Table A-1 continued)

LAB. NO.	RESULTS	METHOD
8222	2.40	2
8222	2.30	1
8242	2.70	2
8242	2.80	1
8421	2.58	1
8421	2.60	2
8512	2.70	1
8512	2.25	2
8623	3.00	1
8723	2.95	2
8723	2.80	1
8922	2.70	1
8922	2.75	2
9111	2.96	2
9111	2.88	1
9113	2.80	1
9113	2.80	2
9523	2.51	2
9523	2.50	1
9713	2.50	2
9713	2.50	1
9716	3.14	1
9716	3.13	2
9811	2.70	1
9811	2.64	2

Table A-2. Sample 2, LAS Acid (0.45 mg/liter)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
1	0.40	1	1213	0.44	2
1	0.52	2	1222	0.45	2
2	0.52	1	1222	0.46	1
2	0.77	2	1311	0.43	1
3	0.44	1	1311	0.43	2
3	0.45	2	1314	0.45	2
6	0.47	1	1314	0.49	1
6	0.47	2	1322	0.40	2
7	0.48	1	1322	0.41	1
7	0.50	2	1511	0.45	1
8	0.42	2	1511	0.47	2
8	0.46	1	1611	0.43	1
1112	0.58	2	1611	0.48	2
1112	0.67	1	1816	0.45	1
1113	0.46	2	1816	0.45	2
1113	0.43	1	1911	0.50	1
1114	0.42	2	1911	0.48	2
1114	0.40	1	1924	0.44	2
1124	0.50	1	1924	0.44	1
1124	0.47	2	2112	0.44	1
1136	0.34	2	2112	0.46	2
1211	0.45	1	2124	0.44	2
1211	0.42	2	2124	0.45	1
1213	0.44	1	2222	0.64	1

(Table A-2 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
2222	0.47	2	3314	0.50	2
2223	0.42	2	3314	0.49	1
2223	0.45	1	3322	0.53	2
2323	0.40	2	3322	0.26	1
2323	0.40	1	3326	0.43	2
2411	0.51	2	3326	0.41	1
2411	0.47	1	3416	0.44	2
2513	0.46	2	3416	0.46	1
2513	0.48	1	3511	0.50	1
2526	0.46	1	3511	0.48	2
2526	0.42	2	3514	0.43	2
2611	0.38	1	3514	0.44	1
2611	0.32	2	3611	0.44	1
2626	0.54	1	3611	0.45	2
2926	0.40	2	3711	0.45	1
2926	0.46	1	3711	0.48	2
3122	0.66	2	3716	0.46	1
3122	0.50	1	3716	0.47	2
3221	0.46	1	3731	0.52	1
3221	0.43	2	3731	0.64	2
3226	0.45	2	4111	0.45	2
3226	0.40	1	4111	0.43	1
3311	0.49	1	4112	0.42	2
3311	0.44	2	4112	0.44	1

(Table A-2 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
4211	0.40	1	5511	0.49	1
4211	0.40	2	5526	0.44	1
4212	0.61	2	5526	0.41	2
4212	0.65	1	5611	0.35	2
4415	0.90	1	5611	0.51	1
4421	0.46	2	5626	0.48	2
4421	0.45	1	5626	0.50	2
4511	0.43	2	5626	0.50	1
4511	0.45	1	5626	0.52	1
4516	0.54	2	5711	0.39	2
4516	0.52	1	5711	0.39	1
4522	0.50	2	5811	0.45	2
4522	0.53	1	5811	0.45	1
4611	0.43	2	5821	0.45	2
4611	0.44	1	5821	0.50	1
4711	0.45	1	5913	0.47	1
4711	0.46	2	5913	0.46	2
5111	0.45	2	5923	0.45	2
5111	0.44	1	5923	0.51	1
5221	0.42	1	6112	0.50	1
5221	0.44	2	6112	0.50	2
5311	0.56	1	6113	0.50	2
5311	0.53	2	6113	0.44	1
5511	0.45	2	6212	0.46	1

(Table A-2 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
6212	0.49	2	7422	0.58	1
6311	0.42	2	7512	0.50	2
6311	0.36	1	7512	0.50	1
6314	0.41	2	7522	0.43	2
6314	0.43	1	7522	0.42	1
6411	0.44	2	7526	0.46	2
6411	0.44	1	7526	0.46	1
6512	0.44	1	7622	0.55	2
6512	0.41	2	7622	0.57	1
6552	0.56	2	7722	0.40	1
6552	0.40	1	7722	0.29	2
6621	0.43	2	7726	0.70	2
6621	0.43	1	7726	0.40	1
6622	0.49	1	7813	0.54	2
6622	0.50	2	7813	0.49	1
6711	0.52	1	7862	0.81	1
6711	0.51	2	7862	0.80	2
6911	0.44	1	7922	0.52	1
6911	0.44	2	7922	0.50	2
7112	0.44	2	7926	0.43	1
7112	0.38	1	8111	0.44	2
7222	0.44	1	8111	0.38	1
7222	0.45	2	8112	0.44	2
7422	0.70	2	8112	0.44	1

(Table A-2 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
8222	0.62	1	9111	0.46	2
8222	0.66	2	9111	0.46	1
8242	0.40	2	9113	0.46	1
8242	0.40	1	9113	0.45	2
8421	0.36	1	9523	0.43	1
8421	0.30	2	9523	0.45	2
8512	0.36	2	9713	0.50	1
8512	0.50	1	9713	0.50	2
8623	0.46	1	9716	0.53	2
8723	0.45	2	9716	0.54	1
8723	0.45	1	9811	0.40	2
8922	0.46	2	9811	0.38	1
8922	0.44	1			

Table A-3. Sample 3, LAS Acid (0.25 mg/liter)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
1	0.18	1	1213	0.22	1
1	0.25	2	1222	0.20	2
2	0.21	2	1222	0.23	1
2	0.32	1	1311	0.22	1
3	0.21	2	1311	0.22	2
3	0.22	1	1314	0.24	1
6	0.21	2	1314	0.23	2
6	0.22	1	1322	0.20	2
7	0.20	1	1322	0.22	1
7	0.20	2	1511	0.20	2
8	0.22	2	1511	0.19	1
8	0.26	1	1611	0.19	1
1112	0.20	2	1611	0.21	2
1112	0.17	1	1816	0.21	2
1113	0.20	2	1816	0.22	1
1113	0.24	1	1911	0.22	1
1114	0.20	1	1911	0.22	2
1114	0.21	2	1924	0.20	2
1124	0.24	2	1924	0.22	1
1124	0.24	1	2112	0.24	1
1136	0.16	2	2112	0.25	2
1211	0.21	2	2124	0.22	1
1211	0.21	1	2124	0.23	2
1213	0.21	2	2222	0.21	2

(Table A-3 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
2222	0.28	1	3314	0.21	2
2223	0.20	2	3314	0.21	1
2223	0.22	1	3322	0.05	1
2323	0.20	2	3322	0.24	2
2323	0.20	1	3326	0.20	1
2411	0.25	2	3326	0.20	2
2411	0.24	1	3416	0.27	2
2513	0.26	1	3416	0.28	1
2513	0.25	2	3511	0.28	2
2526	0.20	1	3511	0.30	1
2526	0.20	2	3514	0.22	2
2611	0.21	2	3514	0.23	1
2611	0.26	1	3611	0.24	2
2626	0.19	1	3611	0.25	1
2926	0.25	2	3711	0.24	2
2926	0.21	1	3711	0.24	1
3122	0.24	1	3716	0.23	1
3122	0.30	2	3716	0.25	2
3221	0.25	2	3731	0.31	1
3221	0.28	1	3731	0.36	2
3226	0.20	1	4111	0.17	1
3226	0.16	2	4111	0.18	2
3311	0.25	1	4112	0.22	2
3311	0.24	2	4112	0.22	1

(Table A-3 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
4211	0.18	1	5511	0.25	1
4211	0.18	2	5526	0.21	2
4212	0.31	2	5526	0.21	1
4212	0.26	1	5611	0.26	1
4415	0.58	1	5611	0.18	2
4421	0.21	1	5626	0.20	1
4421	0.21	2	5626	0.20	2
4511	0.22	2	5626	0.25	2
4511	0.22	1	5626	0.24	1
4516	0.22	2	5711	0.19	2
4516	0.21	1	5711	0.18	1
4522	0.27	2	5811	0.23	2
4522	0.25	1	5811	0.20	1
4611	0.20	2	5821	0.18	2
4611	0.20	1	5821	0.26	1
4711	0.28	2	5913	0.21	1
4711	0.25	1	5913	0.24	2
5111	0.23	2	5923	0.22	1
5111	0.23	1	5923	0.23	2
5221	0.24	1	6112	0.25	2
5221	0.23	2	6112	0.15	1
5311	0.26	2	6113	0.20	1
5311	0.22	1	6113	0.22	2
5511	0.23	2	6212	0.25	2

(Table A-3 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
6212	0.23	1	7422	0.38	1
6311	0.18	1	7512	0.29	2
6311	0.23	2	7512	0.26	1
6314	0.20	2	7522	0.23	1
6314	0.20	1	7522	0.20	2
6411	0.24	1	7526	0.22	1
6411	0.26	2	7526	0.22	2
6512	0.23	1	7622	0.23	2
6512	0.19	2	7622	0.19	1
6552	0.28	1	7722	0.16	1
6552	0.20	2	7722	0.15	2
6621	0.19	2	7726	0.19	1
6621	0.16	1	7726	0.30	2
6622	0.24	2	7813	0.23	1
6622	0.24	1	7813	0.22	2
6711	0.29	2	7862	0.34	2
6711	0.29	1	7862	0.29	1
6911	0.21	2	7922	0.26	1
6911	0.21	1	7922	0.26	2
7112	0.20	1	7926	0.20	1
7112	0.22	2	8111	0.18	2
7222	0.20	1	8111	0.18	1
7222	0.20	2	8112	0.20	1
7422	0.26	2	8112	0.22	2

(Table A-3 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
8222	0.28	2	9111	0.20	1
8222	0.22	1	9111	0.21	2
8242	0.17	2	9113	0.25	2
8242	0.15	1	9113	0.22	1
8421	0.21	2	9523	0.24	2
8421	0.18	1	9523	0.25	1
8512	0.21	2	9713	0.25	2
8512	0.20	1	9713	0.25	1
8623	0.21	1	9716	0.30	1
8723	0.22	2	9716	0.29	2
8723	0.21	1	9811	0.18	1
8922	0.20	2	9811	0.20	2
8922	0.20	1			

APPENDIX B.

GLOSSARY OF STATISTICAL TERMS

A glossary of statistical terms defined as they are used in this report is presented to ensure uniform and complete understanding.

Arithmetic mean	The sum of a series of test results divided by the number of tests in the series.
Median	Halfway point in the readings when they have been arranged in order of size (the middle reading of an odd number of readings, or the average of the middle two for an even number).
Accuracy	The correctness of a measurement, or the degree of correspondence between the results and the true value (actual amount added).
Accuracy data	Measurements that relate to the difference between the average test results and the true value when the latter is known or assumed. The following measures apply:
	Average deviation from true value – Average difference (when always considered as positive) between the mean determination for each laboratory and the true value.
	Average percent deviation from true value – Average of the differences between a laboratory's replicate results and the true value expressed as percentages of the true value.
	Mean error – The average difference with regard to sign of the test results from the true results. Also the difference between the average of a series of test results and the true results.
	Relative error – The absolute value of the mean error of a series of test results as a percentage of the true result.
Precision	A measure of the reproducibility of measurements, or the degree to which the measurements correspond to one another.

Precision data — Measurements that relate to the variation among the test results themselves, i.e., the scatter or dispersion of a series of test results without assumption of any prior information. The following measures apply:

Variance – Sum of squares of deviations of the average test results from the mean of the series divided by one less than the total number of average test results.

Standard deviation – Square root of the variance.

Relative standard deviation (coefficient of variation) – Standard deviation expressed as a percentage of the mean of a series of laboratory results.

Range – Difference in magnitude between the highest and lowest laboratory mean.

Average percent deviation within laboratory – Average of the differences between the replicate results from a laboratory and the mean of their results, expressed as percentage of their mean.

Confidence limits – Limits within which the true mean of the population (the theoretically infinite number of possible replications of the analysis) will lie with a given probability.

95% Tolerance limits – Limits within which one can state with chosen confidence that 95% of the individuals of a population will lie.

APPENDIX C.

TESTS FOR NORMALITY AND REJECTION OF OUTLIERS

Test for normality

The Kolmogorov-Smirnov goodness of fit test was used to determine whether the observations reported could reasonably be thought to have come from a normal distribution. *

Briefly, the test involves computing the observed cumulative frequency distribution (the percent of values less than or equal to each value in the distribution) and comparing it to the theoretical normal cumulative frequency distribution. The point at which the two distributions, theoretical and observed, show greatest divergence is determined. Reference of the value of the divergence to a table of critical values for the Kolmogorov-Smirnov goodness of fit test indicates whether such a large divergence is likely on the basis of chance. If such a large divergence is not likely, the distribution is designated as nonnormal; otherwise the distribution is designated as normal.

Tests for rejection of outliers

1. If the distribution is designated as nonnormal, the suspected outlier (the farthest value from the mean) is rejected only if the distance between it and the mean is greater than three standard deviations; otherwise the suspected outlier is accepted.

2. If the distribution is designated as normal and the sample size is less than or equal to 30, the suspected outlier, the farthest value from the mean, is tested for rejection by a method developed by Dixon. ** Briefly, this test involves computing a ratio that compares the distance of the suspected value from its neighbors to the range of all or most all of the observations (depending on the exact number in the distribution). Reference of the ratio to a table of critical values for test ratios for gross errors indicates whether such a large ratio is likely on the basis of chance. If the ratio is greater than or equal to the critical value, the probability that the suspected outlier is from the sample distribution is small; hence, the outlier is rejected. If the ratio is less than the critical value, the suspected outlier probably came from the sample distribution; hence, the suspected outlier is accepted.

* S. Siegel. Nonparametric Statistics for the Behavioral Sciences. McGraw-Hill Book Company, Inc. New York, New York. 1956. pp. 47-51.

** W. J. Dixon and F. J. Massey, Jr. Introduction to Statistical Analysis, Second Edition. McGraw-Hill Book Company, Inc. New York, New York. 1957. p. 276.

3. If the distribution is designated as normal and the sample size is greater than 30, the suspected outlier is tested for rejection by a method developed by Santner.[+] This method employs the statistic $\frac{\overline{X} - X_o}{s}$, where $\overline{X}$ is the sample mean, X_o is the suspected outlier (the farthest value from the mean), and s is the sample standard deviation. This statistic is compared to a table of critical values to determine whether its value is larger than would be expected on the basis of chance. If the statistic is greater than or equal to the critical value, the suspected outlier is rejected; otherwise, the suspected outlier is accepted.

Application of tests for normality and for rejection of outliers to ARS studies

The test for normality and subsequent test for rejection of outliers are applied to the observed data in two ways; first, to each method for a given substance at a given level of concentration, and then to a given substance at a given level of concentration regardless of method. In either case, it is first necessary to determine whether the original distribution is normal or nonnormal. If the original distribution is designated as nonnormal, method 1 is used to test for rejection of the suspected outlier farthest from the mean. If the suspected outlier is not rejected, no further tests for normality or rejection of outliers are made, and the distribution is designated as nonnormal. On the other hand, if the suspected outlier is rejected, the new distribution, which excludes the rejected observation, is then tested for normality. If the new distribution is nonnormal, the next suspected outlier is tested for rejection by method 1; and this cycle of testing for normality and testing for rejection of outliers continues until a suspected value is not rejected or the test for normality designates the distribution as normal. If the distribution is designated as normal, subsequent tests for rejection of outliers made by method 2 or 3 are the same as if the original distribution had been normal. This case is discussed next.

If the original distribution is designated as normal or a new distribution that was originally nonnormal is designated as normal after the rejection of one or more outliers, and if the number of observations is not greater than 30, then method 2 is used to test for rejection of the suspected outlier farthest from the mean. If the suspected outlier is not rejected, no further tests are made and the distribution is designated as normal. If the suspected outlier is rejected, then the suspected outlier farthest from the mean of the new distribution is tested for rejection and so on until the suspected value of a new distribution is not rejected; when this occurs, no further tests are made and the final distribution is designated as normal. On the other hand, if the number of observations

[+] J. Santner. Personal communication.

in the original distribution is greater than 30, method 3 is used to test the suspected outlier for rejection. If the suspected outlier is not rejected, no further tests are made and the distribution is designated as normal. If the suspected outlier is rejected, then the suspected outlier farthest from the mean of the new distribution, which excludes the rejected value, is tested for rejection. Testing for outliers continued by this method until a suspected outlier is not rejected or the number of observations is no longer greater than 30, in which case method 2 is used for testing for rejection of any remaining suspected outliers.

APPENDIX D.

COMPARISON OF METHODS FOR SIGNIFICANCE OF DIFFERENCE IN PRECISION AND ACCURACY

The methods with respect to precision and accuracy are compared in two ways. In the first case, two methods are compared at a given level of concentration with respect to precision and with respect to accuracy. The variances of the two methods are first compared by the F-test[1] to determine whether there is a significant difference in the precision of the two methods. The means of the two methods then are compared by the t-test[2] to determine whether there is a significant difference in the accuracy of the two methods. The t-test employed is based on the F-test results. These two tests of hypotheses will produce one of the following results.

Outcome 1: $s_1^2 = s_2^2, \overline{X}_1 = \overline{X}_2$

Outcome 2: $s_1^2 = s_2^2, \overline{X}_1 \neq \overline{X}_2$

Outcome 3: $s_1^2 \neq s_2^2, \overline{X}_1 = \overline{X}_2$

Outcome 4: $s_1^2 \neq s_2^2, \overline{X}_1 \neq \overline{X}_2$

In outcome 1, we conclude that no significant difference in precision or accuracy exists between the two methods.

In outcome 2, we conclude that there is no significant difference in precision between the two methods, but there is a significant difference in the accuracy of the two methods; specifically the method whose mean is closer to the true value is the more accurate. In outcome 3, we conclude there is no significant difference in the accuracy of the two methods, but the method with the smaller variance is the more precise.

In outcome 4, we conclude that there is a significant difference in the precision and in the accuracy of the two methods. The method with the smaller variance is the more precise, and the method whose mean is closer to the true value is the more accurate.

In the second case, more than two methods are compared at a given level of concentration with respect to precision and with respect to accuracy. Bartlett's Test[3] is used first to test the hypothesis of equality of variances in order to compare the precision of the methods. If the pre-

cision is the same, the Analysis of Variance [4] is then used to test whether a significant difference exists in the means, in order to compare the accuracy of the methods. If there is a significant difference in the means, Duncan's Multiple Range Test [5, 6] is used to determine which method means differ significantly. If the precision is not the same, then the Kruskal-Wallis One-Way Analysis of Variance by Ranks [7] is used to determine whether significant difference exists in the means, in order to compare the accuracy of the methods.

Once again, there are basically four possible outcomes after the above tests of hypotheses.

Outcome 1: all s_i^2 are equal, all $\bar{X}_i$ are equal

Outcome 2: all s_i^2 are equal, not all $\bar{X}_i$ are equal

Outcome 3: not all s_i^2 are equal, all $\bar{X}_i$ are equal

Outcome 4: not all s_i^2 are equal, not all $\bar{X}_i$ are equal.

In outcome 1, we conclude there is no significant difference in the precision or the accuracy of the methods.

In outcome 2, we conclude there is no significant difference in the precision of the methods; however, at least one method does differ significantly with respect to accuracy, and Duncan's Multiple Range test tells us which methods differ. For example, in comparing four methods, we might conclude $\bar{X}_1 = \bar{X}_2$ and $\bar{X}_3 = \bar{X}_4$ but $\bar{X}_1$ and $\bar{X}_2$ differ significantly from $\bar{X}_3$ and $\bar{X}_4$, or we might conclude $\bar{X}_1 = \bar{X}_2 = \bar{X}_3$ but $\bar{X}_4$ differs significantly from $\bar{X}_1$, $\bar{X}_2$ and $\bar{X}_3$.

In outcome 3, we conclude there is no significant difference in the accuracy of the methods, but the precision is different in at least one method.

In outcome 4, we conclude that both accuracy and precision of the methods differ significantly.

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APPENDIX E.

ANALYTICAL REFERENCE SERVICE MEMBERSHIP

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Alabama State Department of Public Health, Montgomery
Alabama Water Improvement Commission, Montgomery
Arizona State Department of Health, Phoenix
Arkansas Pollution Control Commission, Little Rock
Arkansas State Department of Health, Little Rock
California Department of Water Resources, Sacramento
California State Department of Public Health, Los Angeles
California State Department of Public Health, Air and Industrial Hygiene Laboratory, Berkeley
California State Department of Public Health, Sanitation and Radiation Laboratory, Berkeley
Colorado Department of Public Health, Denver
Connecticut State Department of Health, Hartford
Delaware Water and Air Resources Commission, Dover
District of Columbia Department of Public Health, Washington, D. C.
Florida Department of Agriculture, Tallahassee
Florida State Board of Health, Jacksonville
Florida State Board of Health, Pensacola
Flordia State Board of Health, Winter Haven
Hawaii State Department of Health, Laboratories Branch, Honolulu
Hawaii State Department of Health, Occupational and Radiological Health Section, Honolulu
Idaho Department of Health, Boise
Illinois Department of Public Health, Springfield
Illinois State Water Survey, Champaign
Illinois State Water Survey, Peoria
Indiana State Board of Health, Indianapolis
Iowa State Hygienic Laboratory, Des Moines
Iowa State Hygienic Laboratory, Iowa City
Kentucky State Department of Health, Division of Laboratory Services, Frankfort
Kentucky State Department of Health, Radiological Health Program, Frankfort
Lawrence Experiment Station, Massachusetts
Louisiana State Department of Health, New Orleans
Maryland State Department of Health, Division of Biochemistry, Baltimore
Maryland State Department of Health, Division of Health Education, Baltimore
Maryland State Department of Water Resources, Annapolis
Massachusetts Department of Public Health, Amherst

Massachusetts Department of Public Health, Boston
Michigan Department of Conservation, Lansing
Michigan Department of Public Health, Lansing
Minnesota Department of Agriculture, St. Paul
Minnesota Department of Health, Minneapolis
Missouri Department of Health, Jefferson City
Montana Bureau of Mines and Geology, Butte
Montana Health Department, Helena
Nebraska State Department of Health, Lincoln
Nevada Department of Health and Welfare, Las Vegas
Nevada State Department of Health, Reno
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New Hampshire Water Supply and Pollution Control Commission, Concord
New Jersey State Department of Health, Trenton
New Mexico Department of Public Health, Sante Fe
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New York State Conservation Department, Scottsville
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New York State Department of Health, Division of Laboratories and Research, Albany
New York State Department of Labor, New York City
North Carolina Department of Water and Air Resources, Raleigh
North Dakota State Department of Health, Bismarck
North Jersey District Water Supply Commission, Wanaque
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Tennessee Department of Public Health, Nashville
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Texas State Department of Health, Austin
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Vermont State Department of Health, Barre
Vermont State Department of Health, Burlington
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Virginia State Department of Health, Bureau of Laboratories, Richmond
Virginia State Water Control Board, Richmond
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Washington State Food and Drug Laboratory, Seattle
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Wisconsin Department of Agriculture, Madison

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Albuquerque Department of Environmental Health, Food and Institutional Division, New Mexico
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